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Optimization of Micro and Nanoimprinting

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Abstract

A semi-analytical model is presented for the de-embossing phase of the nanoimprint patterning process. The model is based on established principles of elastic fracture mechanics as developed for fibre-bridged cracking in composites. De-embossing is idealised as a steady-state fracture process, which enables the energy change to be considered by reference to a unit cell of a cylindrical polymer post, de-embossing from an axisymmetric stamp. The model provides predictions of the achievable limits for de-embossing as a function of key geometrical variables such as feature size, area ratio and aspect ratio and material properties such as interfacial adhesion, shear strength, polymer yield strength and the ratio of the elastic moduli of the polymer and the stamp. Process 'maps' have been created showing de-embossing limits. A strong dependence of the achievable aspect ratio on the pattern area ratio and the interfacial shear stress is seen. For polymer yield stresses similar to that of PMMA, the critical interfacial strain energy release rate has little effect on de-embossing. Large area and aspect ratios are predicted to be achievable by keeping the ratio of polymer and stamp Young's moduli between 0.015 and 2.5. The model provides key insights into the physical origins of previously observed limits on the achievable aspect ratios and area ratios achieved by imprint patterning.

Keywords

NIL, nanoimprint, de-embossing, analytical, modelling, process maps

Notation

R = unit cell radius, δ = displacement, z = distance, λ = slip length, τ = shear stress, σ = applied stress, r = radius, f = area fraction, G_{IC} = critical interfacial strain energy release rate, U = strain energy, A = area, E = Young's modulus, V_{sl} = sliding frictional energy, AR = aspect ratio, R_E = Young's moduli ratio.

Subscripts

0-3 = longitudinal regions of the stamp model, a-c = model state, T = total, p = polymer, c = composite of stamp and polymer, s = stamp, yp = polymer yield stress, ys = stamp yield stress, r = radial direction, z = longitudinal direction, rl = residual layer, st = stamp top.

Introduction

Patterning by imprinting is a significant process technology in the rapidly growing field of micro/nano-system manufacturing. First envisioned as a replacement for optical lithography in 1995, nanoimprint has been developed for use in a variety of applications based on its ability to produce 3D imprinted features [1]. The process imprints a malleable resist with a stamp of higher stiffness. On conforming to the desired pattern and depending on the type of polymer used, the resist is solidified, either by reducing the temperature or via ultra-violet exposure. These process steps are shown in Figure 1.

Nanoimprint techniques are now being used to produce components such as lenses, photonic crystal LEDs and display components and as the technology improves, more devices will benefit from its speed and the reduced tooling costs over optical lithography.

Regardless of how well the polymer forms to the stamp, without successful de-embossing, the technique fails. For small feature sizes, this becomes problematic, with attractive surface forces and friction between the sidewalls preventing the stamp from de-embossing, which can cause fracture and deformation of the imprint features [2].

Much of the current process knowledge has been gained empirically. In previous work [3], published data on nanoimprint lithography (NIL) was collected and used to quantify the effects of the process attributes on de-embossing, showing that well-defined limits exist for process metrics such as: aspect ratio, line width and imprint area fractions. The authors suggested that these were a direct result of the mechanisms involved. To extend these limits and increase the capabilities of the technique, a greater understanding of the de-embossing process is needed.

A simple model was presented by Jung *et al.* that described the problem of stamp detachment according to the standard Griffith energy balance of elastic fracture mechanics [4]. The derived equation took into account the total surface area and the interfacial energies of adhesion. However, their work does not explain how process attributes effect de-embossing, such as those indicated by the review in [3]. For instance there is no reference to the shear stress encountered on the sidewalls of posts or trenches due to friction, or the strain energy stored in the polymer and stamp. Other attempts have been made to model the de-embossing step using finite element (FE) models. These research groups reported on:

1. Varying process parameters such as temperature, cooling time, de-moulding velocity and the embossing force to reduce stresses, to help enable detachment of the stamp [5].
2. Optimizing the parameters for a specific structure [6] and calculating the thermal stresses caused by shrinkage [7].
3. Using Atomic force microscopy (AFM) to characterize the adhesive forces between material sets when de-embossing [8].

These works made it clear that there is a lack of general analysis and simulation tools for de-embossing, which may hinder the advancement of imprint-based nanopatterning techniques.

Of all the limited research conducted to date, none offers an analysis of the de-embossing process in an analytical form that could inform process optimization or provide general guidance for the design and optimization of stamps. A simulation model for de-embossing has been created using non-linear transient thermo-viscoelasticity equations. However, due to its complexity it needs finite element methods [9]. To advance the development of nanopatterning techniques, specifically NIL, a largely analytical model would help by allowing trends to be identified and the relative magnitude of the dependencies and effects of different variables to be assessed. In the present work an analytical model has been developed that takes into account the surface attractive forces, as in Jung *et al.*'s model, but also allows for the effects of shear stress and stored strain energy to provide a more detailed analysis, which can then be used to help optimize imprinting process design.

The following sections of the paper will report on the conception and derivation of a semi-analytical model for the de-embossing process. A flow chart is used to explain how the model works. In the results section, 'maps' have been created for given parameter sets indicating the limits for successful de-embossing. These are reviewed in the discussion followed by concluding remarks.

Model Formation

At nano and micrometre dimensions, the stamp and polymer are very similar to a composite material consisting of continuous fibres within a matrix; the stamp features behave as the matrix and the polymer as the fibres, or vice versa depending on the design. Similarly, de-embossing on such small length-scales is similar to the propagation of a crack transversely through a long fibre composite material under tension. Such calculations have previously been performed for fibre pull-out and long steady-state crack growth in such composites and these are the basis for the calculations used herein to model de-embossing [10, 11].

Assumptions

To form an analytical model, the process is divided into the bonded and de-bonded states: when bonded, the displacement on the stamp is assumed to result in uniform strain throughout the model. There are two possible de-bonded states. In the first the critical interfacial strain energy release rate is overcome, but the stamp remains adhered due to the friction on the sidewalls of the polymer posts and adhesion at the top of the polymer post. The second is when all the attractive and frictional energy forces have been overcome. These states are shown in Figure 2.

It is assumed that failure will not occur between the substrate and the residual layer interface. The de-embossing of the stamp and residual layer are modelled as a crack propagating at the interface in steady state conditions; the crack tip state is independent of the crack length. Initially, the residual layer and stamp are well-bonded. For a steady state crack, the energy needed to create the crack is the difference in system energy before and after crack propagation. Assuming the de-embossing of the stamp from the residual layer can be modelled similarly, this energy method can be employed to calculate the energy states before and after de-embossing in a displacement controlled process.

The model is split up into regions whose stress and strain distributions are calculated separately and these are combined in order to calculate the overall strain energy. The model considers an axisymmetric representative element, consisting of a single cylindrical post, with an associated surrounding area of unpatterned material. The unit cell is radius R . The model assumes the polymer has solidified, completely filling the mould. Frictional contact is assumed on the vertical sidewalls of the cylinder and attractive surface forces between the top and bottom of the stamp and polymer faces. Attractive forces on the sidewalls are accounted for within the sidewall friction. The regions and the layout are shown schematically in Figure 2.

To produce a largely analytical model, the following additional idealisations are made:

1. Materials are linear elastic, homogeneous and isotropic.
2. The longitudinal (zz) stresses are much greater than the other stress components, which are assumed to be negligible.

For an incremental applied displacement δ , before the crack propagates, each region experiences an increase in strain energy. Initially, region z_{12} behaves as a composite material with equal strains in the two materials. After crack propagation, only the region $z_{\sigma 1}$ behaves as a composite; elsewhere dissimilar strains exist between the polymer and stamp over the length z_{σ} extending out from the crack surface, where z_{σ} is the slip length. Across this boundary, it is assumed that there is a constant shear stress τ . For a greater displacement, the slip length increases. De-embossing cannot occur until the slip length is equal to or greater than the length of the polymer post. At this point the stress transferred over the top of the post is assumed to be zero and the slip length can be found by

$$z' = \frac{\sigma_0 r}{2\tau f}, \quad (1)$$

where: σ_0 is the stress applied to the top of stamp, r is the radius and f is the area fraction, which can be written in terms of the representative element radii as

$$f = \frac{r}{R}. \quad (2)$$

In addition to the slip length equalling the embedded length of the polymer, another condition must be met for detachment. The adhesive surface energy between the stamp and polymer needs to be overcome; this is quantified as the critical interfacial strain energy release rate G_{ic} . In the model it is assumed that this occurs first to enable slip. This is a reasonable assumption as for practical NIL a low interfacial adhesion must be achieved.

The majority of variables mentioned and to be found in later equations are known, or are easily measured. The τ and G_{ic} values however are dependent on the material types, geometry and surface finish. These properties are usually not known *a priori* and need to be found through experimentation.

Residual layer stress distribution

After the crack has propagated, the stress distribution in z_{23} ; the residual polymer layer below the post feature, changes from a constant stress across the layer into a varying stress, dependent on the depth and radial distance. Initially, a solution derived from bi-harmonic principles was utilized. An example of a similar stress state was found [12]. However, this proved too complex and an alternative approach was used, approximating the stress distribution in the residual layer to that of a semi-infinite elastic half-space loaded by a flat punch. Such a distribution was described theoretically by Boussinesq [13]. These equations have been troublesome to solve except for particular geometries. Love created a solution based on partial and complete elliptic integrals that provides the stress value at a given point in a semi-infinite half-space by pressure applied over a circular area [14]. Such equations have been used in the present work to describe the stress state below the polymer post.

The solution solves for the stresses at finite positions. These discretized values were integrated to calculate the total strain energy of the region, allowing a semi-analytical analysis method. The results were obtained using a MatlabTM script with a previously created function to calculate the partial elliptic integrals [15].

The stress variation in the body has a greater dependency on the r -coordinate than the z -position, with the greatest variation in stress below the polymer post edge. To increase the accuracy of the analysis, the points where stress values are calculated are stepped in the r -direction by logarithmic distributions radiating out from below the post edge so the stress variation is accurately described. Figure 3a shows this distribution while Figure 3b shows the variation in stress for an applied pressure on the residual layer. The script produces the same stress values at the same positions as given by Love. The same script is used to calculate the displacement of the layer. Only the points directly below the post are integrated in the z direction. The mean of these values in the r -direction is used, for the region below the post, as the free surface should have no displacement.

Stamp Top Distribution

Upon the slip length z equalling the length of the polymer post, it is assumed that no stress is transferred over the top of the polymer post. Should G_{ic} also be overcome, the stamp will de-emboss. At this point, the stress distribution in the stamp top; above the features, takes on a stress distribution varying in z and r as in the residual layer. The difference being that instead of a circular punch, which has the applied stress at the centre of an axisymmetrical model, the stamp features behave as a cylindrical punch, applying stress about an axisymmetric line but not at the centre. This stress distribution is most easily obtained by superposition. This is explained graphically in Figure: 4. An equivalent stress distribution to the pressure applied to the stamp top is created by starting with an applied pressure across the entire surface of $\sigma_0(l-f)$, equal to that seen at z_1 in the stamp features. The stress distribution created by a punch of radius r for the same pressure value is subtracted. The remaining stress values describe the correct stress state. The subtracted stress distribution is calculated in the same manner as for the residual layer.

Model formulation

The model is formulated based on a constant displacement boundary condition. For de-embossing to be successful, two conditions need to be met. Firstly, there must be enough energy applied to the system to overcome G_{ic} . Secondly, the complete length of the post must be able to slide relative to the stamp. These two calculations combined with the fixed displacement condition give different initial stress values. Therefore the greater of the two values is used as the defining de-embossing stress.

With the assumptions used to define the de-embossing stress, the slip length limits the stress that can be applied to the system after the interfaces are created to

$$\sigma_{sl} = \frac{2\tau_{z_1}f}{r}. \quad (3)$$

The energy difference between the two states is calculated for each of the regions of the model. The total strain energy before interface de-cohesion is given by

$$U_{03_a} = \frac{\sigma_{0_a}^2 A_T}{2} \left(\frac{z_{01}}{E_s} + \frac{z_{12}}{E_c} + \frac{z_{23}}{E_p} \right), \quad (4)$$

where: U is the strain energy, A_T is the total area of the unit cell, E_s is the Young's modulus of the stamp, E_c is the Young's modulus of the stamp and polymer acting as a composite and E_p is the Young's modulus of the polymer. The strain energy found in the stamp top after de-embossing of the stamp material is described by

$$U_{01_c} = \frac{\pi}{2E_s} \left(\sum_{z_0}^{z_1} \sum_0^R \Delta\sigma_{rz}^2 drdz \right), \quad (5)$$

while the residual layer energy term is

$$U_{23_c} = \frac{\pi}{2E_p} \left(\sum_{z_2}^{z_3} \sum_0^R \Delta\sigma_{rz}^2 drdz \right). \quad (6)$$

Equations 5 and 6 both use the discretized calculations for estimating the stress after the interface has formed. The polymer post energy is

$$U_{p_c} = \frac{\sigma_{0_b}^3 A_p r}{12E_p \tau f^3} \quad (7)$$

and the stamp features energy is

$$U_{s_c} = \frac{\sigma_{0_b}^3 A_s r}{12E_s \tau (1-f)^2 f}. \quad (8)$$

Collectively, the sum of equations 5 to 8 make up the strain energy stored in the system, U_{03_c} , upon formation of the interfaces.

The frictional energy term is dependent on the materials' Young's moduli. Upon de-embossing, if the stamp material is stiffer – such as in TNIL – then

$$V_{sl_s} = \frac{\sigma_{0_b}^3 E_s^2 A_p r (1-f)^2}{12E_c^2 E_p \tau f^3}, \quad (9)$$

whereas if the cured polymer is stiffer – when using a soft stamp as in UVNIL – the frictional energy term is

$$V_{sl_p} = \frac{\sigma_{0_b}^3 E_p^2 A_p r}{12E_c^2 E_s \tau (1-f)}. \quad (10)$$

For the given values, the equation used to solve for the initial stress that must be applied to overcome G_{iC} is

$$\sigma_{0_a} = \sqrt{\frac{(2G_{iC} A_T + U_{03_c} + |V_{sl_s}|)}{A_T \left(\frac{z_{01}}{E_s} + \frac{z_{12}}{E_c} + \frac{z_{23}}{E_p} \right)}}. \quad (11)$$

The calculations used to obtain the stress for constant displacement are derived in a similar method to those of the energy equations: the displacements of each region in the model are added together. Prior to de-embossing in state **a**, the polymer post and stamp features in the region z_{12} are treated as a

composite with equal strain at each cross-section. After de-embossing, in either state **b** or **c**, in region z_{12} , the displacement is solely based on the extension in the polymer post. This is because the stiffer stamp is relaxed after forming a free surface across its face at z_2 and physically, only the polymer post transfers the stress from this point to the residual layer. For a stiffer polymer, the opposite is true, with the stress being transferred through the stamp. Within the residual layer and stamp top the extensions are found using the discretized equations for the regions directly below the polymer post and stamp features respectively. The overall equation to calculate the stress is

$$\sigma_{0_a} = \frac{\delta_T}{\left(\frac{z_{01}}{E_s} + \frac{z_{12}}{E_c} + \frac{z_{23}}{E_p} \right)}, \quad (12)$$

where: δ_T is the total displacement described as

$$\delta_T = \delta_{st} + \delta_p + \delta_{rl}, \quad (13)$$

where: δ_{st} is the displacement in the stamp top directly above the features, δ_p is the displacement in the polymer post and δ_{rl} is the displacement in the residual layer directly below the post.

With differing conditions and de-embossing sequences, a decision tree is needed within the script. The following section describes the decision making process implemented.

Process tree

De-embossing is dynamic by nature. To create equations that describe the problem statically, a decision process is used, switching between equations and limits describing the different conditions. The model can then solve for multiple inputs and calculate which outcome will succeed. Figure 5 shows a schematic of the process tree. This is implemented as a Matlab script.

The yield strength failure criterion uses the stresses calculated at the base of the polymer post and at the top of the stamp features prior to the slip length equalling the post height; state **b** shown in Figure 2. In state **c**, the stress transferred across the polymer post top is zero, reducing the de-embossing stress. In state **b** however, stress is transferred across the post top with the stamp features and polymer post behaving as a composite. In this state, a greater stress is created and is found by

$$\sigma_{0_b} = \frac{2\tau E_c z_{12} f}{E_s r(1-f)}, \quad (14)$$

which is the equation for slip length in state **b** rearranged and assuming $z_{sl} \approx z_{12}$.

To enable the model to give useful results, attribute values similar to those used in NIL need to be chosen.

Attribute values

To allow comparison between the process maps, a default set of attributes are used. Of these, three will be varied at any one time for comparison. The majority of these have been chosen based on values regularly found in the field of NIL. The default Young's moduli and yield stress values will be based on those of Silicon and Polymethylmethacrylate (PMMA) for the stamp and polymer respectively as they are widely used. The values for τ and G_{IC} are not as easily characterized. Both are dependent on the material and geometry of the stamp. Anti-sticking layers (ASLs) may also be used. It has been reported in published articles that G_{IC} values in the range of 0.249-3.64 J/m² have been achieved by experiments investigating the adhesion between stamp and UV curable polymer [16-18]. The variation is due to different ASLs or materials used. For τ , a value of 0.1 MPa is chosen. Reported values in the composite literature for the maximum interfacial shear stress between the fibres and matrix vary from 26-45 MPa [19-22]. This is the maximum value at the surface and for fibre pullout and tends to have an exponential decline, making the average value somewhat less. The intention in composite research is usually to create a strong bond; making τ as high as the yield shear stress. However, for de-

embossing, where τ should be as low as possible, no experimental results have been found. It is reasonable to expect the imprinting process and the use of ASLs reduce the shear stress by two orders of magnitude, comparable to the observed reduction in G_{iC} . The default attribute values used are displayed in Table 1.

The aspect ratio AR is described as the length of the post (z_{12}) compared to the diameter of the post ($2r$). The Young's moduli ratio R_E compares the polymer to the stamp material. Some examples will be shown in the following section for a few parameter variations. These will be examined further in the discussion.

Results

The following process maps illustrate de-embossing contours of a chosen variable, dependent on the parameters selected for the axes variables. In Figure 6 the model is used to compare how achievable aspect ratios and volume fractions depend on the shear stress (τ). As expected, it can be seen that de-embossing becomes more difficult for higher τ values and for greater values of AR and f . With increasing τ , a greater applied stress is needed to overcome the frictional energy. This is also true for increasing AR or f as both increase the post-wall surface area that the shear stress acts upon.

For the same axes, varying G_{iC} produces the map shown in Figure 7. At low values of G_{iC} the model follows the curve controlled by the bridged-crack strain energy release rate (state **b**), with the post material failing due to the interfacial friction when achieving constant displacement. This is the normal de-embossing process expected for the default attributes chosen and is seen for all f values when G_{iC} is below 13.3825 J/m^2 . However, when there is not enough energy to overcome G_{iC} , de-embossing fails. Physically, this results in the polymer delaminating from the substrate and is displayed graphically as an extremely low aspect ratio.

Within a very narrow band of G_{iC} values, a step change occurs, in which the model switches between providing enough energy to overcome the adhesive surface energy between the stamp/polymer boundary and enforcing constant displacement. For greater f values, a larger G_{iC} can be tolerated. However, the effect is minimal, changing the value by a few $1 \times 10^{-3} \text{ J/m}^2$. Lower critical G_{iC} values have been recorded by using a lower σ_{yp} value than that assigned in **Error! Reference source not found.**

Figure 8 shows the variation of achievable area fraction (f) with respect to polymer yield stress (σ_{yp}) and Young's moduli ratio (R_E). For a given σ_{yp} the map indicates which f values are achievable. It is noticeable that for a typical soft polymer yield stress of 10 MPa , a wide range of area ratios, from 0.01 to 0.5 are achievable if R_E is 2.9×10^{-4} . De-embossing becomes significantly more difficult and hence needs a higher yielding polymer for larger area ratios. When the polymer becomes stiffer than the stamp: $R_E > 1$ i.e. when the Young's modulus is greater than silicon, de-embossing becomes much more difficult. An interesting outcome of the model is there are minima in the yield stress values for area ratios below 0.5 .

A similar map is obtained when the achievable aspect ratio (AR) is assessed with respect to σ_{yp} and R_E . Figure 9 shows AR values of up to 20 can be de-embossed with a σ_{yp} of 20 MPa and a R_E between 1.5×10^{-2} and 2.5 . It also clearly shows σ_{yp} minima for aspect ratios of 5 or less; similar trends to those for f . Again, de-embossing is more easily achieved at R_E values below or close to unity for high aspect ratios.

Discussion

The graphs clearly show dependencies for variables that enable de-embossing. A limit in achievable aspect ratios that was seen to occur from the grouping of experimental results by Balla, Spearing & Monk [3] can be realised easily from Figure: 6. However, the graph provides more useful information. A decrease in shear stress would increase the aspect ratio achievable as a greater post heights would increase side-wall area for friction to act upon. Similarly, decreasing the area ratio has the same effect; decreasing the post wall surface area. It is interesting to note that to achieve the observed maximum

aspect ratios of 10 in [3] in the example presented here, the shear stress must be less than 10 MPa. For the value of 0.1 MPa; the predefined value in Table 1, an aspect ratio of 73 should be achievable. Given that an aspect ratio of 10 is the greatest aspect ratio at micro and nanometre levels to be reported, this suggests either:

1. the sidewall roughness of the stamps used and the surface attraction along the sidewall is able to cause a larger shear stress than assumed by the authors,
2. Other mechanisms, not captured by the model, are involved.
3. greater AR values are achievable, but as yet these have not been fully explored.

Realistically, the shear stress is not constant along the post. Also, in reality the stamp needs to be 'peeled' from the edges to allow air to enter into what would otherwise be a vacuum. The peeling process and the presence of a vacuum at the top of the post makes it likely that the effective shear stress would indeed be significantly higher than that assumed in the model: the peeling process angling the stamp protrusions causing a horizontal force and the vacuum the top of the polymer post creating a back pressure.

The graph depicting de-embossing for varying critical strain energy release rate values shows a sudden switch between been attached and de-embossed. Such a switch is defined by Jung *et al.* in their work looking at the issue solely in free energy terms [4]. However, the model presented in this paper also shows that the switch between stick/slip occurs in a very narrow field of 13.3825-13.3830 J/m². This transition behaviour is not seen for lower strain energy release rate values, such as those obtained using anti-sticking layers. When G_{iC} is 0.5 J/m² or less, the model predicts that there should be no issues with de-embossing and that it is not dependant on the strain energy release rate i.e. its effect is not as important as the sliding friction on de-embossing. For the set of values used in Table 1, the surface energy therefore is less important in the de-embossing process. Should the polymer yield stress be lower than the PMMA value, then de-embossing will become more dependent on the G_{iC} value. An example is shown in Figure 10 in which all the values used in the model are the same as for Figure 7, except σ_{yp} is 10 MPa; 57 MPa lower than for PMMA. It can now be seen that the stick/slip transition occurs at a lower level of 0.298 J/m², values similar to those found experimentally.

De-embossing systems currently have a finite number of materials available to use for moulds and resists, partially due to growing out of the lithography process but also because of the process requirements. This model opens up the possibility of using fictitious values for the Yield strengths and the Young's Moduli of the moulds and resists to see what effect they have on the process and whether it may be beneficial to take their values into consideration when developing new materials. Figures 8 and 9 show the area and aspect ratio plots against polymer yield stress and the ratio of Young's moduli are very similar in shape. To achieve high aspect ratios, which would enable the technique to be used to produce a greater variety and/or more efficient devices, it is beneficial to have a Young's moduli ratio near unity. The same is seen for high values of area ratio, as would be needed to increase the data storage in hard drives when using discrete track recording (*DTR*) or bit pattern media (*BPM*) designs. For area ratios below 0.5 and aspect ratios below 5, the model suggests that the materials with a significantly lower Young's modulus; in the order of 4-5 times lower, may be de-embossed with a lower required material yield stress. This behaviour is associated with the effect of the Young's modulus on the strain energy; at low f values, there is a greater volume of stamp than polymer in the slip length region.

Conclusions

The model has been used to explore how the various material properties and process variables interact to control the achievable aspect ratios and area fractions for the de-embossing phase of imprint patterning. Simplifying assumptions have been made to describe the process so that a semi-analytical model could be created that describes the trends with key variables. This model successfully determines whether de-embossing occurs for various inputs. The model shows there is a very strong dependence of the achievable aspect ratio on the pattern area ratio and the interfacial shear stress. For the critical strain energy release rate values obtained using fluorinated coatings and current standard polymers, it is unlikely that failure to de-emboss will occur due to adhesion for post radii on the order

of 100 nm. However, for smaller post diameters and lower polymer yield stresses it becomes increasingly important to minimize the interfacial adhesion value to enable stamp separation. To reduce the yield stress value of the polymer for de-embossing and therefore enable a greater range of materials to be used, the adhesion, as quantified by the interfacial strain energy release rate should be kept to a minimum. Large area ratios and aspect ratios are more easily achieved by maintaining the polymer/stamp Young's moduli ratio (R_E) in the range 0.015 to 2.5.

Due to the limitations imposed by simplifying the de-embossing step to enable it to be described mainly by analytical means, the model is able to predict trends for variations in parameters but cannot be relied on to provide precise values for when de-embossing occurs. More detailed finite element (FE) models, such as those presented in [5-8, 23] are appropriate for the analysis of specific cases. It also does not take into account viscoelastic properties that have been reported in polymers when de-embossing. Nevertheless, the current work provides guidance as to the trends associated with choices of material and process variable and the relative criticality of such choices. Furthermore the modelling is consistent with and provides quantitative insight into the mechanisms behind earlier observations of trends and limits in experimental studies of imprint patterning techniques [3].

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References

1. Chou, S.Y., P.R. Krauss, and P.J. Renstrom, *Imprint of sub-25 nm vias and trenches in polymers*. Applied Physics Letters, 1995. **67**(21): p. 3114-16.
2. Atasoy, H., et al., *Novel thermoplastic polymers with improved release properties for thermal NIL*. Microelectronic Engineering, 2011. **88**(8): p. 1902-1905.
3. Balla, T., S.M. Spearing, and A. Monk, *An assessment of the process capabilities of nanoimprint lithography*. Journal of Physics D: Applied Physics, 2008. **41**(17): p. 174001 (10 pp.).
4. Jung, G.Y., et al., *Improved pattern transfer in nanoimprint lithography at 30 nm half-pitch by substrate-surface functionalization*. Langmuir, 2005. **21**(14): p. 6127-6130.
5. Song, Z., *Study of Demolding Process in Thermal Imprint Lithography via Numerical Simulation and Experimental Approaches*, in *Mechanical Engineering 2007*, Louisiana State University: Baton Rouge.
6. Worgull, M. and M. Heckeke, *New aspects of simulation in hot embossing*. Microsystem Technologies, 2004. **10**(5): p. 432-437.
7. Worgull, M., M. Heckeke, and W.K. Schomburg, *Large-scale hot embossing*. Microsystem Technologies, 2005. **12**(1-2 SPEC ISS): p. 110-115.
8. Yuhua, G., et al., *Study of the demolding process - implications for thermal stress, adhesion and friction control*. Journal of Micromechanics and Microengineering, 2007. **17**(1): p. 9-19.
9. Worgull, M., et al., *Modeling of large area hot embossing*. Microsystem Technologies, 2008. **14**(7): p. 1061-1066.
10. Aveston, J., A. Kelly, and G.A. Cooper, *Single and multiple fracture (Single and multiple fractures in brittle matrix fibrous composites, discussing fracture energetics, stress-strain curves and hysteresis effects)*, in *The Properties of Fibre*

- Composites* 1971, IPC Science and Technology Press Ltd: Teddington, Middx, England; United Kingdom. p. 24-26.
11. Zok, F.W. and S.M. Spearing, *Matrix crack spacing in brittle matrix composites*. *Acta Metallurgica et Materialia*, 1992. **40**(8): p. 2033-2043.
 12. Filon, L.N.G., *On the Elastic Equilibrium of Circular Cylinders under Certain Practical Systems of Load*. *Philosophical Transactions of the Royal Society of London. Series A*, 1902. **198**: p. 147-233.
 13. Boussinesq, J., *Application des potentiels: à l'étude de l'équilibre et du mouvement des solides élastiques*. 1885, Paris: Gauthier-Villars.
 14. Love, A.E.H., *The Stress Produced in a Semi-Infinite Solid by Pressure on Part of the Boundary*. *Philosophical Transactions of the Royal Society of London. Series A*, 1929. **228**: p. 377-420.
 15. Igor, M., *Elliptic Integrals of three types and Jacobian Elliptic Functions*, 2005, Matlab Central.
 16. Taniguchi, J., et al., *Measurement of adhesive force between mold and photocurable resin in imprint technology*, in *International Microprocesses and Nanotechnology Conference 2001*, Japan Soc. Appl. Phys: Shimane, Japan. p. 4194-7.
 17. Houle, F.A., et al., *Antiadhesion considerations for UV nanoimprint lithography*. *Applied Physics Letters*, 2007. **90**(21): p. 213103.
 18. Jang, E.-J., et al., *Effect of surface treatments on interfacial adhesion energy between UV-curable resist and glass wafer*. *International Journal of Adhesion and Adhesives*, 2009. **29**(6): p. 662-669.
 19. Bennett, J.A. and R.J. Young, *The effect of fibre-matrix adhesion upon crack bridging in fibre reinforced composites*. *Composites Part A: Applied Science and Manufacturing*, 1998. **29**(9-10): p. 1071-1081.
 20. Chohan, V. and C. Galiotis, *Interfacial measurements and fracture characteristics of 2D microcomposites using remote laser Raman microscopy*. *Composites Part A: Applied Science and Manufacturing*, 1996. **27**(9): p. 881-888.
 21. Galiotis, C., et al., *Interfacial measurements and fracture characteristics of single and multi-fiber composites by remote laser Raman microscopy*, in *The Symposium on Fiber, matrix, and interface properties*, C.J. Spragg and L.T. Drzal, Editors. 1996, ASTM: Phoenix, AZ, USA. p. 19-33.
 22. Piggott, M.R. and Y. Xiong, *Direct observation of debonding in fiber pull-out specimens*, in *The Symposium on Fiber, matrix, and interface properties*, C.J. Spragg and L.T. Drzal, Editors. 1994, ASTM: Phoenix, AZ, USA. p. 84-91.
 23. Worgull, M., et al., *Modeling and optimization of the hot embossing process for micro- and nanocomponent fabrication*. *Microsystem Technologies*, 2006. **12**(10-11): p. 947-52.